

Effects of iron phthalocyanine on the inner pressure of MH/Ni battery

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Abstract Effects of iron phthalocyanine (FePc) on the inner pressure of MH/Ni batteries during charging were examined. Experimental results show that the battery with appropriate quantity of FePc displays a much lower inner pressure under charging and overcharging than the battery without FePc, especially the battery with 1 mg FePc exhibits the slowest increasing speed of inner pressure and the best charging efficiency and overchargeability.

Keywords: inner pressure, MH/Ni batteries, iron phthalocyanine, hydrogen storage alloy, electrochemical catalyst.

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The inner gas pressure of the battery beyond 1.01×10^6 Pa can cause a release of gas from the safety valve for a normal sealed cell, leading to a drying out of electrolyte solution^[1], and gradually decreasing the performance of the battery until finally destroying it.

During overcharging, oxygen is produced rapidly on the nickel electrode, and it is necessary to eliminate the oxygen and restrain the rising speed of inner pressure so as to improve the performance of MH/Ni battery.

Phthalocyanine (FePc) is a kind of compound with a big-ring which can chelated with metal ion such as iron, cobalt and nickel. As a functional material, ring-metalated phthalocyanine compounds exhibit a strong ability of activating oxygen^[2], and excellent electrocatalytic ability for the reduce reaction of oxygen^[3–6]. We have reported the effects of phthalocyanine compounds on the performance of MH/Ni battery previously^[7]. In this paper, the effects of the addition of FePc to negative electrode with various dosages on the inner pressure of MH/Ni battery were measured and reported.

1 Experimental

FePc was dissolved in ethanol and the solution exhibited a color of oxford blue. The solution was deposited on the negative electrode alloy with various dosages of FePc (without FePc (1); 1 mg FePc (2); 2.5 mg FePc (3)).

1.1 Preparation of nickel electrode

A foamed nickel plate was used as the nickel electrode substrate, and β -Ni(OH)₂ powder and small amount of Co and CoO were employed as the positive electrode materials. The positive electrode (82 mm \times 40 mm \times 0.68 mm, 8.2 g) was carefully selected to ensure the capacities of them located at (1.70 ± 0.05) A \cdot h.

1.2 Preparation of hydride electrode

The alloy powder with the composition of $\text{MnNi}_{3.6}\text{Co}_{0.7}\text{Mn}_{0.4}\text{Al}_{0.3}$ (MI: La-rich mishmetal) and the appropriate quantity of FePc mixed to form a mixed powder. HPMC and PTFE aqueous binder were then added to the mixed powder. The mixture adhered

to a punched nickel strip, then dried, was pressed and cut to form the negative electrode ($115\text{ mm} \times 42\text{ mm} \times 0.33\text{ mm}$, 9.1 g).

1.3 Preparation of test batteries

Each AA size battery was constructed by the positive electrode and the negative electrode as well as a piece of non-woven polyamide separator. A solution of 6 mol/L KOH and 1 mol/L LiOH was as the electrolyte.

The experimental batteries were prepared by using three different negative electrodes with various dosages of FePc and their nominal capacity was $(1.70 \pm 0.05)\text{ A} \cdot \text{h}$.

1.4 Test of inner pressure

The inner pressure of the battery during charging and discharging was measured by an inner pressure test system^[8] at $23\text{--}25^\circ\text{C}$. The battery was sealed in a chamber and the gas generated during charging was led to a pressure sensor through a hole on the top of the battery.

2C (3.4 A) pulse charge/discharge cycles of the batteries were carried out by the following scheme: charging at 3.4 A for 15 min , resting for 15 min , then discharging at 3.4 A until the voltage decreased to 1.0 V . The cycle number can reach 500.

1C (1.7 A) charge/discharge cycles of the batteries were carried out by the following scheme: charging at 1.7 A for 72 min , resting for 15 min , then discharging at 1.7 A to 1.0 V until to 150 cycles.

The inner pressure of battery was measured at 0.4C (0.68 A), 1C and 2C , respectively, and the state of different terminative capacities was equal to 200% or 150% of the normal capacity. During the whole charge/discharge process, the internal pressure of each sample battery was recorded in sequence.

2 Results and discussion

2.1 Inner pressure of batteries after 2C pulse charge/discharge cycles

Fig. 1 shows the inner pressure of the three AA size MH/Ni batteries after 2C pulse charge/discharge

cycles when charged at 0.4C up to 200% of the normal capacity.

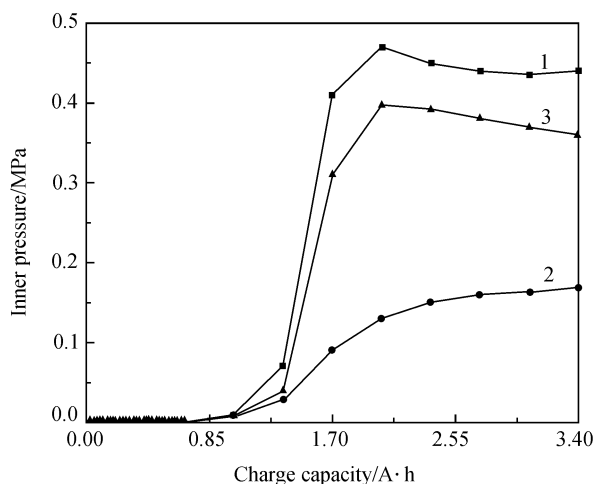


Fig. 1. Inner pressure comparison at 0.4C (0.68 A) charging. 1, Battery without FePc; 2, battery with 1 mg FePc ; 3, battery with 2.5 mg FePc .

It is obvious that the inner pressure increases sharply when charging up to 100% of the normal capacity. Battery 1 without FePc displays the fastest increase of inner pressure, which reaches 0.47 MPa when just charging to $2.04\text{ A} \cdot \text{h}$ (120% of normal capacity). While the pressure of battery 2 with 1 mg FePc is near to equilibrium at 160% of the normal capacity. And up to 200% of the normal capacity, the inner pressure of battery increases only to 0.16 MPa . This phenomenon indicates that in this overcharge period, from 160% to 200% of the normal capacity, the rate of gas evolution equals that of gas consumption. The pressure climbs no longer when the inner pressure reaches 0.44 and 0.39 MPa for batteries 1 and 3 respectively. These two values are much higher than those of battery 2.

Fig. 2 indicates the changes of inner pressure with charging capacity at 1C rate up to 150% of the normal capacity. Similar to the 0.4C rate charging process, the inner pressure of battery 1 increases sharply when just charging to 66% of the normal capacity, while the increase of inner pressure of batteries 2 and 3 becomes obvious only when the charging capacity approaching 100% of the normal capacity. After

that the inner pressure increases more slowly but does not reach equilibrium as emerged when charging at 0.4C rate.

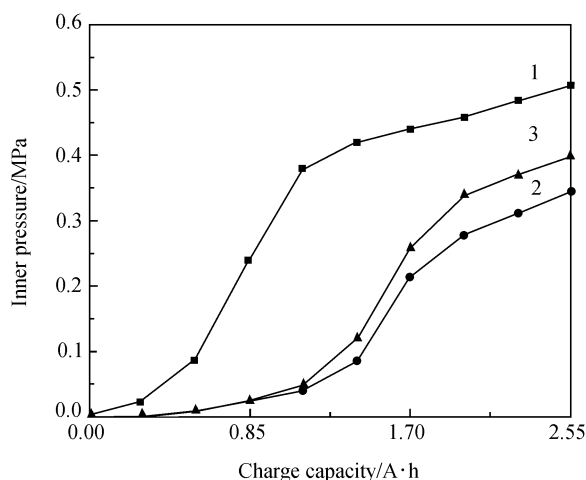


Fig. 2. Inner pressure comparison at 1C (1.7 A) charging. 1, Battery without FePc; 2, battery with 1 mg FePc; 3, battery with 2.5 mg FePc.

The pressure is greatly reduced by adding FePc and the charging efficiency of the battery is significantly improved. But as a kind of organic compound with a big-ring, FePc has the poor conductivity, which may be the reason that battery 3 with much more FePc exhibits a higher pressure than that of battery 2.

2.2 Inner pressure of batteries before and after 1C cycles

The batteries were charged up to 200% for three cycles at both 1C and 2C rate before and after 150 cycles, and then discharged at the 0.4C rate to 1 V at 25°C. It can be seen that the charging inner pressure becomes high after 150 cycles (fig. 3). This result is in agreement with the early report^[9]. A slight increase of the pressure is observed after cycles as compared with the pressure before cycles for battery 2. Also a significant increase in the inner pressure is observed when charging at the 2C rate for the three batteries, especially for battery 1.

Figs. 4 and 5 show the pressure changes with charge capacity at 1C and 2C rate respectively. It can be seen that pressure of all the batteries increases with the charge capacity after cycles. Battery 1 has the

highest inner pressure both before and after cycles. When charging at 2C rate after cycles, the increase of the pressure is so sharp that it reaches to 2.16 MPa when charging to 150% of normal capacity (2.55 A·h). On the other hand, although battery 3 has the lowest inner pressure initially, its climbing speed is even higher than that of battery 2 after cycles. This means that battery 3 with 2.5 mg FePc in the negative electrode has a better initial activity, but a worse cycle stability. The inner pressure of battery 2 increases much more slowly than that of other two batteries after

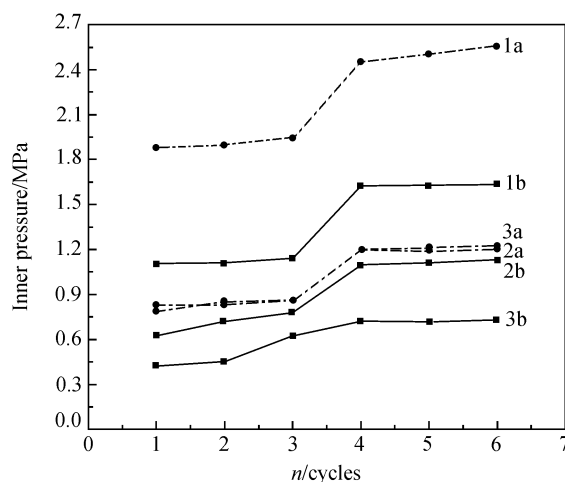


Fig. 3. Inner pressure comparison before and after 150 cycles. 1, Battery without FePc; 2, battery with 1 mg FePc; 3, battery with 2.5 mg FePc. a, After cycles; b, before cycles. The first three cycles with 1C rate; the last three cycles with 2C rate.

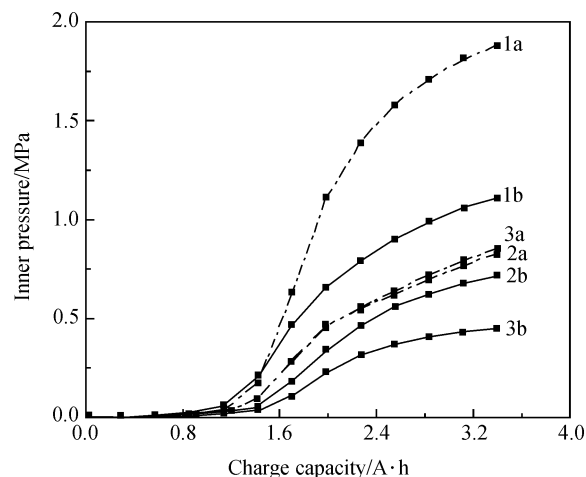


Fig. 4. Inner pressure comparison at 1C (1.7 A) charging before and after 150 cycles. 1, Battery without FePc; 2, battery with 1 mg FePc; 3, battery with 2.5 mg FePc. a, After cycles; b, before cycles.

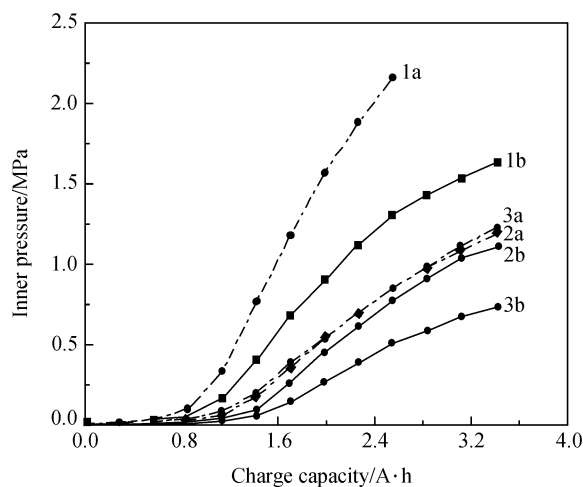
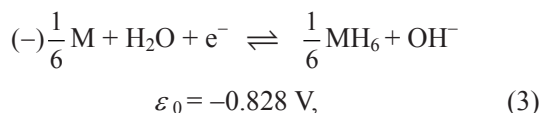
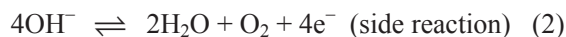
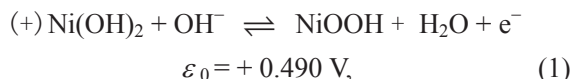


Fig. 5. Inner pressure comparison at 2C (3.4 A) charging before and after 150 cycles. 1, Battery without FePc; 2, battery with 1 mg FePc; 3, battery with 2.5 mg FePc. a, After cycles; b, before cycles.

the cycles. That is to say, the addition of 1 mg FePc in the negative electrode displays a more significant improvement for decreasing the inner pressure.

2.3 Reaction mechanism

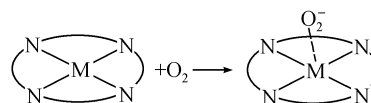
In an MH/Ni battery, some electrochemical reactions are given as follows:



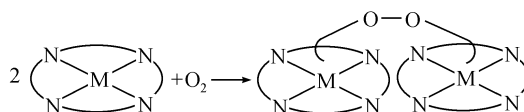
The side reactions (2) and (4) constitute the oxygen circulation inside the battery. In the presence of oxygen, MH/Ni battery is a three-phase system consisting of the solid matrix, liquid electrolyte and a gas phase. During charging and overcharging, oxygen is generated at the nickel/electrolyte interface and may evolve into the gas phase after exceeding its solubility in the electrolyte solution. The oxygen can then be transported, via the liquid and gas phases from the nickel to MH electrode where the oxygen gas may

dissolve in the electrolyte and be reduced at the MH/electrolyte interface. Such a process forms an internal oxygen cycle in a recombinant battery like the MH/Ni battery^[10]. The accumulation of oxygen in the gas phase will lead to a battery pressure build-up.

A phthalocyanine compound of transition metal is constituted of a big heterocyclic ring in planar structure and a transition metal atom at the center of plane. The conjugated molecule exhibits a high flatness. The catalytic reaction with oxygen can take place at the direction of axial^[11,12].



OR



From the results above, the adding of FePc can catalyze the reducing reaction of the oxygen, decrease the reduce potential of oxygen. At the same time, as a carrier, FePc also plays a role in transmitting the oxygen from the positive electrode to the negative one. All these are helpful in increasing the speed of oxygen elimination, and therefore decreasing the inner pressure.

3 Conclusion

The inner pressure of MH/Ni battery increases sharply during overcharging or charging at the high rate. But it can be reduced remarkably by adding FePc to the negative electrode, especially with an appropriate quantity of FePc (1 mg per battery).

FePc, as an electrochemical catalyst and a transmitting carrier of oxygen, can improve the charge efficiency and the overcharge tolerability of the MH/Ni battery.

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